MODELING STUDY OF PCBs IN THE HOUSATONIC RIVER PEER REVIEW

Modeling Framework Design
Final Written Comments

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May 24, 2001

RESPONSE TO CHARGE FOR THE HYDRODYNAMIC MODELING PEER REVIEW

I. General Overview of Response

INTRODUCTION

The modeling study of PCBs in the Housatonic River is a substantial undertaking, and this is reflected in the Modeling Framework Design (MFD) report and the associated Quality Assurance Project Plan (QAPP). These documents address a complex problem, in terms of the modeling objectives, and in some ways succeed in developing a defensible modeling approach. Complexities of the site and of the aquatic and terrestrial ecosystem, along with numerous uncertainties, data limitations, and other constraints, makes the Housatonic River PCB contamination as difficult a problem as I have seen. It has required substantial effort for the Peer Review Panel to absorb and understand all of the elements of the MFD. The opportunities for dialog with the EPA modeling team have been too limited to be productive. A more open dialogue amongst the peer reviewers, and between the panel and the modeling team, would have greatly facilitated this process. I encourage EPA and GE to revise the process prior to subsequent iterations of peer review.

I perceive the value of peer review at this stage of the project (conceptual design) to be fairly limited. There are two reasons for this. First, you hire a modeler, not a model. By that I mean the choice of model and modeling approach depends upon who is doing the work. We have all invested years of effort developing expertise in at most a handful of models, gaining skill in their use through site-specific applications. The choice of models and modeling approaches that comprise the MFD are essentially complete once the modeling team is selected, and this bridge has been crossed. There has appeared to be little flexibility on the part of EPA or their modeling team to consider alternatives to the 3-model construct defined by the MFD. I hope that is not the case, because the Panel has attempted to advance constructive comments and suggestions, with the objective of improving the scientific defensibility and likelihood of success of the modeling exercise.

Secondly, it can be difficult to judge the success of modeling based upon prior review. The success of modeling is judged in terms of predictions, not formulations. At best, we can compare the overall MFD and it's elements to models and modeling approaches which have succeeded or failed in the past. However, it is possible that alternative models and approaches may perform as well (or better). I have struggled with this issue through much of the MFD, particularly with aspects of the MFD considered "avante garde" by the standards of most water quality modelers. These include:

- the incorporation of the food web bioaccumulation simulation within an ecosystem model,
- kinetic models of PCB partitioning to detrital (sediment) and planktonic organic carbon,
- parallel models for abiotic and biotic PCB transport and fate processes, and
- the direct use of SEDFLUME experimental data to parameterize sediment resuspension properties.

Much of the Panel's deliberation at the Public Meeting focused on the seemingly excessive complexity of these and other aspects of the MFD. In general, we concluded that adopting complex or avante garde approaches to modeling required specific justification or rationalization, and that this generally had not been provided by the MFD. The defense of the avante garde is made by the modeling team:

> New applications and linkages of existing models are not necessarily undesirable. Development of a successful modeling framework for a challenging problem such as the evaluation of baseline conditions and alternative PCB remediation strategies for the Housatonic River has the potential to significantly advance the body of knowledge for contaminant transport and fate modeling in riverine systems.[1]

[1] *EPA Response to Peer Review Panelist Questions on the Housatonic River Modeling Framework Design* (April 12, 2001).

By itself, this is not an adequate justification for the complexity of the modeling framework.

There are risks which accompany innovation; most obviously, the risk of failure. Prior success may be the best indicator of a favorable outcome. This conservative philosophy is one basis of the engineering discipline. Many of the comments submitted by Quantitative Environmental Analysis (QEA) on November 30, 2000 critical of the MFD are a reflection of this conservatism. A second risk is that if too much effort is devoted to making a new application succeed, some other more fundamental task may be overlooked or shortchanged, possibly jeopardizing the project. A project such as this one, where the timelines and schedule appear to be carved in stone, is the wrong place to get creative. The tolerance for risk is much higher in the research and development environment than it is in the regulatory arena. Since the stated objectives of this project fall entirely within the latter, it is necessary to consider the "What if this doesn't work?" contingency in the event of failure. I have concluded that constructive criticism of the avante garde approach can best take the form of suggesting what additional data collection, analytical and modeling efforts are appropriate as contingencies. Contingency plans need to be built into the MFD.

EPA and Marasco Newton both emphasized the importance of prioritizing recommendations in our final written comments. I believe the Panel's most important recommendation, is to continue a monitoring program during and after remediation in the upstream river reaches. This should include monitoring flow, TSS/POC/DOC, and dissolved and particulate PCBs on a regular basis, at 3-5 locations in the Study Area including the confluence, bridges, and Wood's Pond dam. To this should be added annual sampling of target fish species, for determination of trends in lipid and PCB body burdens.

SUMMARY OF CHARGE

The following are comments in response to the Peer Review Panel's "Summary of Charge", which otherwise do not seem to fit in response to the Peer Review Questions which follow:

- ***Are the available data sufficient for development of models of the hydrodynamics, sediment transport and the chemistry, fate and transport, and bioaccumulation of PCBs in the Housatonic River?***

The project data described in the MFD are insufficient for calibration and verification of several significant processes. Data are lacking for:

Tributary boundary conditions
Bed load of sediment and PCBs
Erosion Rates (including aggrading bars/terraces and banks)
PCB partitioning
Lower food web PCB concentrations
Diet (predator/prey relationships)

- ***Are the processes in the final models calibrated/validated to the extent necessary for prediction of future conditions?***

Accuracy of both event and long-term simulations may be difficult to demonstrate due to lack of necessary validation data ("big event" sampling, and data quality and comparability issues involved with measuring long-term contaminant decline).Without such data, significant model processes will not be adequately constrained by calibration to ensure reliability of forecast predictions.

- ***How sensitive are the models to uncertainties in the descriptions of the relevant processes?***

All models are sensitive to uncertainty! They are most sensitive to unexpected/unknown uncertainties, which unfortunately cannot be estimated. In terms of PCBs predicted in water and sediment, the most significant (known) uncertainties are associated with the following processes:

Loadings (PCBs and suspended sediments)
Initial conditions for sediment PCB concentrations
Resuspension and deposition fluxes (especially at high shear stresses)
Sediment bed mixing and diffusion
Partition coefficients
Net loss of PCBs during overbank flood conditions

For PCB concentrations predicted in fish, additional uncertainties include:

Plankton and benthos biaccumulation relationships (i.e., BAF and BSAF predictions)
Fish prey, dietary contaminant assimilation relative to food, and elimination rates
Sediment feeding selectivity and invertebrate uptake and elimination rates

II. Response to Peer Review Questions

In considering the foregoing general issues and evaluating the EPA documents, the Peer Review Panel shall give specific consideration to the following questions. As modeling activities proceed, additional specific questions may be identified the panel to address.

A. <u>Modeling Framework and Data Needs</u>

1. Do the modeling frameworks used by EPA include the significant processes affecting PCB fate, transport, and bioaccumulation in the Housatonic River; and are the descriptions of these processes in the modeling framework(s) sufficiently accurate to represent the hydrodynamics, sediment transport, PCB fate and transport, and PCB bioaccumulation in the Housatonic River?

In general, the MFD does identify the significant processes affecting PCB fate, transport, and bioaccumulation in the Housatonic River. The process descriptions are also generally adequate; as mentioned, some of the process models are excessively complex. Weaknesses in the process descriptions are noted for the following:

- Erosion of river bank solids and PCBs (apparently this cannot be described?)
- Deposition or other losses for PCBs transported onto the flood plain,
- Partitioning of PCB transport and fate into "abiotic" and "biotic" processes,
- Food web predator/prey linkages and feeding descriptions at the base of the food web,
- Surficial sediment mixing,
- Chemical transport and fate descriptions in EFDC, and
- Some alternatives are offered to the organism-level bioaccumulation formulations and parameterization used in AQUATOX**,**
- Detrital carbon sorption kinetics (i.e., desorption kinetics) model used in AQUATOX.

I would suggest discarding "Non-partitioning of PCBs" and wind-driven transport processes from conceptual model.

AQUATOX ecosystem model

The "classical" or conventional approach to modeling chemical bioaccumulation in food chains and food webs (as defined by Weinenger, et al.,1983; Nordstrom, 1976; Connolly and Thomann, 1984; Thomann, 1989; Gobas, 1993), is based on a mass balance applied at the whole-organism level. Mass balance equations for representatives of each trophic level are coupled in a prescribed manner by the specification of predator-prey relationships. These can be simple or complex, including such factors as change in diet with age, season, and/or location. It can be demonstrated, either by observation or via sensitivity analysis, that bioaccumulation of highly-hydrophobic chemicals is very sensitive to predator-prey relationships. This is especially true for organisms consuming a diet including both benthic and pelagic food items, because of the large gradient in hydrophobic chemical exposure observed between water and sediment.

The accuracy and certainty of the predator-prey specification is constrained by the data available to describe organism diet, typically gut content analyses. This approach of specifying predator-prey relationships can be criticized for (at least) the following:

- Gut content data reflect the predator-prey relationship at a particular time and place. Depending on the circumstances, this data may be extremely variable. Collecting this data is labor-intensive and logistically difficult; therefore, even in the best case, there is usually not enough gut content data to adequately define the predator-prey relationship in a continuous manner. Although other analytical methods (nitrogen isotope ratios, for example) may overcome some of the discontinuity problem, the general problem of uncertainty in this specification of predator-prey relationships remains.
- Gut content data reflect the predator-prey relationship at the time of sampling, and have no predictive (forecasting) power other than assuming that tomorrow will be like today. We know this not to be true, therefore bioaccumulation forecasts made with specified predator-prey relationships will be inherently uncertain.

Several food web models have been developed which couple the bioaccumulation process with ecosystem simulation of predator-prey dynamics. AQUATOX, BASS, and the MCM are examples of this type of coupled ecosystem/bioaccumulation model. The ecosystem model is used to simulate the density and/or biomass of food web organisms. The density of different organisms serves to modify the specified prey preference of predators according to abundance. The goal of this approach is to develop food web models which overcome both of the limitations identified above, (namely) the use of insufficient, discontinuous measurements to specify predator-prey relationships, and the lack of forecasting ability. Unfortunately, there are a number of problems with this approach as well:

- A great deal of site-specific data are required to properly constrain an ecosystem simulation, much more than will exist for an aquatic ecosystem unless great resources are brought to bear;
- Many fish, especially top predators, may have specific prey preferences and are essentially insensitive to prey abundance;
- Unless confirmed by gut contents data (the need for which was supposed to be avoided), ecosystem simulation of predator-prey relationships may be no more (and possibly less) accurate than use of gut contents data to directly specify predator-prey relationships;
- Especially worrisome is the possibility that an unconstrained ecosystem simulation could shift the modeled predator-prey relationship towards an unrealistic feeding scenario, for example a planktivorous fish feeding on detritus or benthos due to the relative abundance of biomass. An error of this sort apparently occurred in the AQUATOX application to PCBs in Lake Ontario (Park, August 1999), when parameterization error caused amphipod biomass to drop below the minimum level for feeding by smelt. This error in the ecosystem simulation had an effect on PCB bioaccumulation which cascaded up through the trophic levels.
- I am aware of no research to demonstrate that bioaccumulation predictions made by ecosystem-based food web models are more accurate and/or reliable than specified food web models;
- The forecasting ability of ecosystem-based food web models depends upon whether the forcing functions (climate, nutrient and energy fluxes, fisheries management, invasive species, ...) can be anticipated. Since this is not likely, the best that can be done is to use the ecosystem model for

bounding analysis, something that can probably be done directly using life history data for the food web organisms of interest.

QEA has commented that AQUATOX ecosystem dynamics (biomass change with time) will be unconstrained by data. They argue it is better to specify diet based upon site data and literature, and deal with uncertainty in the diet specifications. The Peer Review Panel lacks an ecological modeler. I know I am not, so I really cannot evaluate whether the planned collection of biomass data will adequately constrain the simulation of ecosystem dynamics in AQUATOX. AQUATOX calibration/validation (QAPP 4.7) does include biomass as a calibration goal.

If population densities of trophic levels modeled in the AQUATOX food web cannot be confirmed by available biomass data, trophic linkages based upon both abundance and prey preferences will be unconstrained in the absence of site-specific diet studies. The ecosystem dynamics incorporated in AQUATOX are otherwise irrelevant for the Housatonic River application. The uncertainty in bioaccumulation predictions (including pelagic vs. benthic contaminant accumulation routes) may be large (to an unknown extent), especially over annual and longer time scales. It is crucial for bioaccumulation modeling that the trophic linkages be realistic during simulation; an ecosystem modeling approach doesn't appear to guarantee this. The model must do better than "produce realistic ecosystem dynamics based on general principles", it must do the best job possible to describe the predator-prey relationships in the ecosystem. The conventional engineering modeling approach appears to be simpler and less uncertain.

To sum this up, there may be little to gain by using the ecosystem-based modeling approach in the Housatonic River. For this application, it adds unnecessary complexity to an already difficult modeling problem. It also specifies the collection of biomass data which is otherwise irrelevant to the problem at hand. These aspects are distractions from the stated modeling objectives. Ecosystem model simulation has no direct utility in the context of the modeling objectives; it is only relevant in terms of establishing trophic (predator/prey) relationships. My recommendation is that the ecosystem dynamics simulated by AQUATOX be constrained or disabled so that predator-prey interactions in the food web remain consistent with data from other similar ecosystems, the literature, and applicable site-specific gut content studies, and that data should be collected to validate the trophic pathways in the food web model.

AQUATOX Model Description

I am quite familiar with AQUATOX and the contaminant-specific research it incorporates, yet I found the model description in the MFD baffling at times. Examples:

- AQUATOX mass balance equations account for contaminant transfer associated with deposition and erosion, but apparently not pore water diffusion nor groundwater infiltration. Is this correct? These may be significant processes for sediment-water contaminant exchange under low flow conditions.
- Does AQUATOX not account for accumulation of DOC in sediment pore water as a result of detrital carbon decomposition? This differs from several other diagenesis models I have reviewed, where detrital carbon undergoes transformation to DOC as well as CO_2.
- Are inorganic solids (D1, D2 and D3) treated as state variables in AQUATOX? Do they adsorb PCBs? Is this based on assuming an organic carbon content?
- I am not sure why AQUATOX calculates non-equlibrium partition coefficients for invertebrates (eqn. 53) and fish (eqn. 54). Is this done to address slow biphasic chemical elimination? Otherwise, it seems to make AQUATOX inconsistent with other bioaccumulation models for invertebrates (Morrison, Landrum) and fish (Gobas, Thomann). Why not calculate equilibrium partition coefficients from organism lipid content?
- Doesn't AQUATOX use a better calculation of respiration rate (species-specific bioenergetic) than the allometric cited from Thomann?

I recommend that this section of the MFD (Appendix D) as well as the QAPP be revised, to make it easier to understand how AQUATOX is being applied in the Housatonic River.

Other Comments and Recommendations for AQUATOX

- A whole literature exists of correlations for K_{oc} (KOM in equations 49 and 50). For the sake of consistency, it would be worth considering results from studies where K_{oc} was determined simultaneously for both particulate and dissolved organic carbon phases, such as Eadie et al. (Chemosphere, 1990).

- Elimination rates (equation 82): There has been much good elimination rate data published for PCBs and other HOCs. Data from Sijm and van der Linde (1995), de Boer et al. (1994), and Sijm et al. (1992) should be added to the training set for this regression.

- Regarding the use of Swackhamer et al.'s kinetic model for phytoplankton bioaccumulation, it would be worthwhile to update AQUATOX to reflect the use of organic carbon as the sorbing matrix instead of lipid (Skoglund and Swackhamer, ES&T, 1999). Also, the exposure time and growth rate parameters in that model should be coupled to the relevant variables in AQUATOX. Of course, the phytoplankton BAF predictions must themselves be validated to data.

- Heather Morrison's steady-state model should be considered for modeling invertebrates; it appears to do about the best job in matching the BAFs and BSAFs observed for PCB congeners.

AQUATOX Sorption Kinetics

AQUATOX incorporates a kinetic model for sediment partitioning, as opposed to the equilibrium partitioning model used in most contaminant transport and fate models. The limitations of the equilibrium partitioning assumption for modeling hydrophobic organic chemicals have been discussed extensively in the literature, and have been demonstrated via model simulations (Lick et al., 1997; Song et al., 1977), yet the assumption remains popular for a number of reasons. First, it greatly simplifies and speeds the solution of the mass continuity equations in the model. Second, it requires only the measurement of "standard" water quality measurements for parameterization. And third, no generally-accepted kinetic model has emerged from 20 years of process experimentation and modeling. The kinetic model used in AQUATOX is Karickhoff's reversible 2-compartment model. This model considers desorption as occurring simultaneously from slow and rapid sorbent sites, each characterized by first-order kinetics. Whether this approach is any better than equilibrium partitioning (or simple modifications to equilibrium partitioning; for example, QEA's Hudson River model) is debatable, and should be tested in the model. As noted by Wu and Gschwend (1986 and 1988), desorption rate constants are NOT constant over the duration of the desorption process, a complexity arising from the distribution of particle sizes in suspended solids, as well as from non-uniform sorbate concentrations (Gong and DePinto, 1988). Currently, most process modelers seem to prefer distributed parameter or heterogeneous radial diffusion models. Incorporation of such kinetic models is well beyond the capabilities of AQUATOX, as it requires high spatial and temporal resolution, treatment of sediment hysteresis, and solution of stiff partial differential equations.

There also appears to be an error in Equation 66, the estimate of desorption rate k_2. Using a K_p value appropriate for hexachlorobiphenyl, I get a desorption rate of 10^{-5}/d. This contrasts with desorption rates of 0.1/d (Song et al., 1997) and 0.05/d (Lick et al., 1997). Maybe Equation 66 estimates desorption rates in units of $seconds^{-1}$? Otherwise the difference is too great to reconcile.

EFDC Model Description

Process representation for PCB transport/fate in EFDC are overly-simplistic, both in relation to "state of the art" and the partitioning representations in AQUATOX. Simple EFDC process representations seems inappropriate, for example lumped first-order loss rates and the lack of 3-phase partitioning.

Modeling Framework: EFDC (Abiotic) vs. AQUATOX (Biotic) Components

Separation of biotic and abiotic components of PCB transport and fate is a potentially significant weakness. This separation is artificial, and appears to be motivated by the selection of models that (without modification) are not truly appropriate for this application. There is no such thing as biotic and abiotic PCBs, per se. This creeps into the description of EFDC, for example:

> EFDC will model abiotic components and AQUATOX will model both biotic and abiotic components.
>
> This code modification (to EFDC) will allow, for example, the capability to define seasonal and spatial differences in the organic carbon fraction of each solids class to account for winter_summer differences in phytoplantkon that are included as a component of field measurements of grain size distributions, TSS and POC. Specific modeling of volatilization and microbial degradation in EFDC is not envisioned other than as lumped first_order rates.

This separation is not as clean a separation of processes as, for example, transport/fate vs. bioaccumulation, which has been successfully applied in PCB models for the Hudson River and Green Bay/Fox River. Using separate programs to model abiotic and biotic transport and fate processes is untested; success of this approach has not been demonstrated.

I think there are a number of altematives to the PCB transport and fate model that should be considered by the modeling team. These include:

- Modeling all PCB transport/fate in EDFC, which would appear to require only the incorporation of a 3-phase organic carbon equilibrium partitioning model.
- Choose an alternative model which can simulate both biotic and abiotic processes;

Likewise, there are viable alternatives for modeling PCB bioaccumulation:

- Model only PCB bioaccumulation in AQUATOX (the only "biotic" PCB transport and fate processes unique to AQUATOX are sorption kinetics and accumulation by periphyton and macrophytes, neither of which have been demonstrated to be of significance in the Housatonic River application)
- Choose an alternative food web bioaccumulation model more consistent with this engineering application.

I expect that the effort necessary to develop an alternative modeling framework (based, for example, on EFDC and AQUATOX) would probably be less than that proposed for handling the complex linkages that are required by the framework described in the MFD.

Model Framework Linkages

The model linkages between solids and organic carbon sorbent state variables, are a potential weakness of the modeling framework design, and potentially a significant source of error. While these linkages do solve the problem of incompatible state variable definitions between models, there are a number of problems which are not adequately addressed in the MFD:

- Several of the linkages may not conserve mass
- Several of the linkages are based on empirical relationships, which may be only weakly predictive

> The key requirement for the model linkage is the necessity to maintain a careful mass balance of flow and constituent loads between HSPF, EFDC and AQUATOX.

State variable linkages for solids/sorbents between models are complex procedures (models, in effect): grain size vs. organic/inorganic particle states, BOD vs. POC, etc. "Linked" state variables (example: organic carbon sorbents) must be calibrated/confirmed like other predicted state variables. The intricacy of several of these linkages may lead to a great deal of effort and potential for errors. Is the empirical approach for establishing linkages good enough to use in a quantitative modeling framework? Seems like this has not been addressed, yet it may be significant in overall uncertainty of modeling. Such linkages have apparently been applied in the past in conjunction with HSPF; hopefully, this would provide some basis for discussion in the MFD.

A related concern is how deposition and resuspension velocities are aggregated in both space and time (QAPP 4.9.3.6). In particular, it is not clear how the aggregation scheme will handle erosion and deposition occurring within the same averaging period and/or aggregated segment. Will the individual (gross) deposition and resuspension velocities be averaged separately for transfer to AQUATOX, or will net particle velocity (deposition - resuspension) be averaged/transferred? This detail of the aggregation and linkage schemes must be properly designed to ensure that the correct interaction of sediment and suspended solids in AQUATOX.

Data linkages from EFDC to AQUATOX

The QAPP goes through the state variable linkages in some detail, which is good. However, some further clarification is necessary:

- Equations 4-3 and 4-4: How good are the spatially- and temporally-dependent estimates of TOC:TSS? Don't you really want the POC:TSS ratios?
- Equation 4-3: Shouldn't the TOC:TSS ratios be different for each PIM size class?
- PIM export/import: From this I assume that AQUATOX must partition PCBs onto PIM? I could not confirm this from the documentation. How are these partition coefficients determined, since by definition these particles have no organic carbon content?
- POM deposition/resuspension: Cohesive solids deposition and resuspension velocities are applicable to the POM associated with fine-grained cohesive solids; they would not for phytoplankton (unless river phyto are much smaller than diatoms). Is POM a state variable independent of phytoplankton? Again, this is something I could not confirm in the AQUATOX documentation

While the description of EFDM-AQUATOX linkages in the QAPP(4.9.3) refers to erosion and deposition fluxes, in fact it is vertical particle velocities which are linked (?).

Data linkages from HSPF to AQUATOX

Similarly, there is need for clarification in the QAPP regarding these linkages:

- Equations 4-8 and 4-9: Is there an error in these equations (what happened to BOD)?
  From the mingling of model state variables and data I cannot tell, but I suspect these linkages do not conserve mass. If so, doesn't this violate an objective of the MFD? Regardless, POC and DOC boundary conditions must be calibrated and validated as predicted states.

Model Uncertainty Analyses

There is some discussion of uncertainty analysis in the AQUATOX description. To be useful in the context of the linked modeling framework, however, such analyses must consider all aspects of the transport, fate, and bioaccumulation simulation, including uncertainty in external forcing functions and state variable linkages. Model uncertainty should be addressed by a combination of:

- Monte Carlo analysis; preliminary, similar to sensitivity analysis (AQUATOX description makes use of too few realizations to be quantitative)
- Bayesian Monte Carlo; informative parameter distributions based on calibration (may be computationally intensive for dynamic simulations)

- Alternative bounding calibrations (although this approach can be abused by subjective application)

2. Based upon the technical judgment of the Peer Review Panel:

a. ***Are the modeling approaches suitable for representing the relevant external force functions (e.g.. hydraulic flows, solids and PCB loads, initial sediment conditions, etc.), describing quantitative relationships among those functions, and developing quantitative relationships between those functions and PCB concentrations in environmental media (e.g., water column, sediments, fish and other biota, etc.)?***

Complete and accurate loadings of solids, organic carbon, and especially PCBs is probably the most critical factor in the success of the mass balance models. HSPF is not suitable (unless confirmed) for prediction of upstream PCB loadings. The modeling team apparently agrees, and has chosen to use PCB loading estimates based upon conventional regression models instead. This is the most suitable and accepted method for representing contaminant loadings, assuming that the necessary flow-weighted sampling has been conducted. This, of course, should be reflected in revision of the MFD.

b. ***Are the models adequate for describing the interactions between the floodplains and the river?***

It is unclear whether the proposed linkage will correctly predict the net transport of PCBs from the river to the flood plain. In their presentation, QEA showed results of mass balance analyses suggesting that the magnitude of this interaction could be estimated based on PCB concentrations measured in the river during floods. Such estimates would at least constrain the PCB transport interactions between the floodplains and the river.

c. ***Are the models adequate for describing the impacts of rare flood events?***

Other models, based on the same tau-epsilon resuspension relationships, have been demonstrated to accurately describe sediment transport impacts of flood events (excluding bank slumping, overbank flow, and small-scale bed features). However, model adequacy must be demonstrated in each system due to great variability. I am not sure that the magnitude of the flow events sampled in 1999 is large enough for such demonstration; data is available for one 2-5 year flood. Obviously, data for a larger event would be valuable, and such monitoring should be considered if possible.

It is not clear how the resuspension data provided in the Gailani et al. (September 2000) report will be used to generate the spatially-distributed resuspension properties required to model the sediment bed of the river and pond. The report points out that considerable variation of sediment bulk properties and erosion rates were observed above Woods Pond, and that further effort would be required to develop a sediment mapping of these properties and test them with a sediment transport model. This recommendation should be pursued, in order to develop a complete data set for resuspension properties. How well this is done may determine the success or failure of the sediment transport simulation.

d. ***Are the models adequate for discriminating between water-related and sediment-related sources of PCBs to fish and other biota?***

The question is poorly posed. Food web bioaccumulation models <u>can</u> simulate PCB accumulation via sediment and water exposure routes, given appropriate information regarding diet. See comments regarding AQUATOX food web simulation under Question 1.

3. Again, based upon the technical judgment of the Panel, are the spatial and temporal scales of the modeling approaches adequate to address the principal need for the model - producing sufficiently accurate predictions of the time to attain particular PCB concentrations in environmental media under various scenarios (including natural recovery and different potential active remedial options) to support remedial decision-making in the context described above in the Background section? If not, what levels of spatial and temporal resolutions are required to meet this need?

Spatial Resolution of Models

The spatial segmentation of the water column in AQUATOX appears reasonable, but the same segmentation applied to the surficial sediment bed may be too coarse. Cursory examination of the sediment PCB distribution maps, indicates that concentrations deviate in a systematic manner between mid-channel and near-shore regimes, longitudinally within subreaches, and with depth and location within Woods Pond. This suggests that additional sediment segmentation may be warranted. The relationship between erosion and deposition regimes as predicted by sediment transport model, and the AQUATOX sediment segmentation should also be considered. If not, then AQUATOX may erroneously associate low (or high) PCB concentrations with sediments being resuspended from a particular EFDM sediment segment.

MFD does not adequately consider how long-term hindcast and forecast predictions will be constructed, although these issues are critical to the outcome (Gailani et al., 1996; Velleux and Endicott, 1996). Usually modelers don't think about this until model calibration/verification is complete; it is generally too late then!

Another issue to consider is the methodology for long-term validation:

> Following calibration of the models using data from 1991_2000, the models will then be validated by assigning initial conditions based on data sets collected during 1979_1980. Model validation will be based on a long_term simulation beginning in 1979 and ending in 1990. The long_term simulation from 1979_1990 is intended to provide validation of the models with an independent data set. Continuation of the validation period of the simulation through 1991_2000 then provides an additional rigorous test of the predictive capability of the models using a continuous simulation against data available within a 20_year period. If the models can successfully reproduce the observed data sets over a 20_year period, then the credibility of the model for projecting the potential impacts of alternative remedial action scenarios >50 year decadal time scales will be greatly enhanced.

A reasonable approach. One question about this: What is the contingency plan in the event that the long-term hindcast fails to validate the models? How and where will corrective action take place?

4. Is the level of theoretical rigor of the equations used to describe the various processes affecting PCB fate and transport, such as settling, resuspension, volatilization, biological activity, partitioning, etc., adequate, in your professional judgment, to address the principal need for the model (as defined above)? If not, what processes and what resolution are required?

There are various possible process representations for PCB transport and fate, which vary in terms of complexity and theoretical rigor. However, most models have adopted representations which are consistent with conventional principles: organic carbon-based equilibrium partitioning in both particulate and dissolved phases, two-film resistance volatization using temperature-dependent Henry's constants, a well-mixed surficial sediment layer,

reductive dehalogenation of specific congeners above a saturation concentration, and molecular diffusion from pore water. As previously noted, assumptions of equilibrium partitioning when applied to PCB desorption from resuspended sediments is a potentially significant weakness of most models.

Models of PCB transport and fate, and underlying theory, are not sufficiently robust that parameter values determined a priori can account for all of the site-specific variability that is observed in critical model parameters. This is not a weakness of the models specifically, rather an acknowledgment that all transport and fate models are imperfect representations of chemical behavior in an extremely complex system.

In terms of PCB transport and fate, the issues of resolution and processes in questions 3 and 4 can best be addressed by taking advantage of the redundancy offered by EFDM and AQUATOX. It seems likely that EFDC and AQUATOX predictions of water and sediment concentrations will diverge. This will result from differences in spatial/temporal resolution, and from differences in the transport/fate processes (and their formulation) included in each simulation. Since these models are using different process descriptions, applied at different resolutions, to model the same PCB mass balance, a comparison of their predictions offers an objective test. Do the predictions agree? Why or why not? Which model performs better? It is extremely important to understand both the magnitude of divergence in predictions and their underlying causes. The same PCB state variable needs to be run in both models, however, something the MFD fails to define:

> Since only selected congeners will be simulated, AQUATOX will not simulate total PCBs and the results generated by AQUATOX will not be compared to field observations of total PCBs.

I think it is very important that both EFDC and AQUATOX model at least one consistent PCB state variable. Also, note the importance of verifying constant congener distribution; if distribution varies, chemical parameters for total PCB will not be constant.

Sediment Mixing and Diffusion Processes

In all reviews of sediment mixing processes I have seen, bioturbation is primarily attributed to the activities of benthic invertebrates. Benthic feeding by fish is mentioned by several authors as a possible mixing mechanism, but the extent and intensity of this factor over time is highly uncertain. Attempting to relate sediment mixing to observed carp feeding is tenuous at best. In fact I suspect that the cause of bioturbation really doesn't matter, as in any case the process is parameterized in the models as the depth of the surficial mixed layer, "background" resuspension, and lumped pore water diffusion. Some additional consideration should be given to the 15 cm mixed depth: what is the rationale for this value? Can it be independently confirmed?

On the other hand, there appear to be inconsistencies in the MFD and the model documentation, regarding how molecular diffusion, bioturbation, and groundwater infiltration/percolation are represented in the transport/fate models. Are these modeled as distinct processes, or are they limped into a single transport term?

5. What supporting data are required for the calibration/validation of the model on the spatial and temporal scales necessary to address the principal need for the model (as defined above)? What supporting data are required to achieve the necessary level of process resolution in the model?

I believe that the modeling team is well aware of the data required for model calibration and verification. My only comment specific to this question, is that the description of AQUATOX somewhat trivializes the importance of site-specific calibration.

Calibration and Verification of AQUATOX

Considerable effort is required to calibrate partitioning, particle transport, and especially bioaccumulation processes in a PCB transport and fate model. The parameterization and empirical relationships used to estimate parameter values, as presented in the AQUATOX documentation, should be viewed as prior estimates which are then updated through the calibration process. "Little calibration will be necessary for ecosystem variables in AQUATOX" conflicts with my own experience. Models of PCB transport and fate, and underlying theory, are not sufficiently robust that parameter vaulues determined *a priori* can account for all of the site-specific variability that is observed in critical model parameters. This is not a weakness of AQUATOX specifically, rather an acknowlegement that all transport and fate models are imperfect representations of chemical behavior in an extremely complex system. Statements that little calibration will be necessary in either Woods Pond or upstream river reaches seem unlikely. River systems impacted by in-place pollutants are challenging at the least, as demonstrated by efforts to model PCB dynamics in the upper Hudson River and the Fox River.

AQUATOX makes use of a variety of chemical parameter correlations based upon the octanol-water partition coefficient (equations 49-54, 69-70, 72, 75, 78, 82). These correlations are commonly used to generalize laboratory or field observations of hydrophobic organic chemical parameters, usually under specific controlled or site-specific conditions. As such, they are an acceptable means of generating initial (prior) estimates of chemical parameters for transport, fate and bioaccumulation models. However, adjustment of these estimates is usually necessary as part of the model calibration process; if the data available for validation is suitably constraining, adjustment is almost inevitable. It is not clear from the model description whether AQUATOX allows ready calibration of these parameters, or whether such calibration is anticipated by the modeling team.

I am also somewhat concerned that calibration and validation of bioaccumulation predictions in AQUATOX depend primarily upon predictions of PCB concentrations at the top of the food chain:

> The final confirmation will be in the ability to simulate the observed PCB concentrations in the key fish species.
>
> The test of the validity of this approach will be how effects from the lower food web are integrated into the predicted fish concentrations, for which there is a substantial data set.

This may leave important aspects of the bioaccumulation predictions at lower trophic levels untested and unconstrained, including those which resolve sediment versus water column contaminant exposure and tropic accumulation pathways. I would prefer that calibration and validation consider predictions at all trophic levels to be important, as this would better constrain the model.

Data should be collected to validate the trophic pathways in the food web model. This was not done because:

> Labor_intensive gut analyses and studies of depth of disturbance over seasons was clearly beyond the scope of this site investigation.

I tend to question this, given the extent of soil and sediment sampling performed for this study.

Sediment PCB Data Analysis and Use in Models

What is most striking to me about the maps of PCB distribution in soil and sediment, are the high concentrations (and presumably mass) of PCBs in the river banks. Given what I presume to be this enormous inventory of PCBs in direct proximity to the river, I wonder whether bank erosion might not represent a worse-case scenario for PCB transport and exposure. As I understand it, erosion and slumping of the river bank cannot be resolved or represented in the sediment transport model? Some consideration should be given to how such an event could be simulated.

Aggregation of sediment PCB data should be based on :

- organic carbon normalization;
- deposition regime of sampling location;
- as well as river mile and grain size factors, which were discussed.

The methodology for determining initial conditions for PCB sediment concentrations in 1979, for the hindcast verification, should be discussed. The first sediment PCB measurements were made in 1979-80. Are these data comparable to current measurements, in terms of sampling resolution and analytical methods? If not, won't bias in specification of initial conditions for the hindcast be a problem for long-term validation?

PCB Partitioning

Use of Kp, when you mean Koc, is a pain. Greater consistency would improve the document. The prevalent usage of PCB data normalized to dry weight in sediment is inconsistent with the models, which are representing partitioning to organic carbon/matter.

Inconsistencies in the partitioning data presented in the MFD strongly suggest that additional data be collected to support calibration of PCB partition coefficients in water (including seasonality & range of POC values) and sediment. The modeling team should also look at the range of partition coefficients obtained using a 3-phase (dissolved/POC/DOC) partitioning calculation, to see whether such a model is capable of simulating the range of observed partition coefficients.

The following are two tables with some selected values for PCB partition coefficients in sediment and water. These could be greatly expanded, if desired. The point is that by comparing the range of these values to partition coefficients measured in the Housatonic River, some judgements can be made regarding their quality and representativeness.

PCB partition coefficients measured in sediment

literature source	log K_d	log K_{poc}	log K_{doc}
Di Toro et al. (ES&T, 1985)	5.1	6.6 (cites range of field data as 4.2 - 6)	
Hunchak-Kariouk et al. (ES&T, 1997)		4.6	4.7 - 5.6
Brownawell and Farrington (Geochimica..., 1986)	3 - 4.4		
Velleux and Endicott (JGLR, 1994)		6.35	5.35
QEA (Hudson River, 1999)		5.6 (reversibly sorbed PCBs)	

PCB partition coefficients measured in water column

literature source	log K_d	log K_{poc}	log K_{doc}
Eadie et al. (Chemosphere, 1990)		5.8	3.9
Velleux and Endicott (JGLR, 1994)		6.35	4.35
QEA (Hudson River, 1999)		5.6 - 6.3	

Regarding the low values of sediment Kp, I intended to look at the range of partition coefficients obtained using a 3-phase (dissolved/POC/DOC) partitioning calculation, but then I ran out of time.

The issue of whether phase separation of sediment samples has been done by filtration or centrifugation remains. The response to Peer Review comments says:

> Most of the samples were centrifuged to collect the pore water, a procedure recognized as leaving organic material in the suspended phase.

However, this conflicts with the memos provided from Rich DiNitto, which indicate that filtration predominated.

6. Based upon your technical judgment, are the available data, together with the data proposed to be obtained by EPA, adequate for the development of a model that would meet the above referenced purposes? If not, what additional data should be obtained for these purposes?

The available data, and data collection planned by EPA, are generally consistent with the information required to develop the PCB transport, fate, and bioaccumulation models. There is not an abundance of data for PCBs in the water column or biota, however, and there appear to be some problems with the quality of dissolved PCB measurements. Several other specific weaknesses are evident:

- Data to support empirical state variable linkages - The model linkages for solids and organic carbon states depend upon many observations from which correlations must be constructed. From what I have seen (scatter plots of all TSS and TOC data), the data may not be available to support this approach.
- Loading data
- Partition coefficients
- Diet data to define trophic interactions and benthic/pelagic pathways
- Spatial and seasonal variability of PCB concentrations in plankton and benthos
- Sediment mixed layer thickness

III. Specific Comments on the Modeling Framework Design Report and/or the Quality Assurance Project Plan.

Some much-needed clarity would be gained by changing some of the nomenclature used in the MFD and QAPP. The best examples I can identify are:

Historical PCB sources -	replace with “in-place PCBs”
Partition coefficients -	Use of Kp, when you mean Koc, is a pain. (Greater consistency would improve the document.)

MFD should make better use of long-term data when developing the conceptual model and identifying important processes. For example, use the GE YOY fish PCB data and 1979-80 sediment PCB data to show changes in PCB concentrations over time. Analysis of long-term data is helpful to determine whether PCB dynamics are controlled by internal (sediment inventory) vs. external (loadings, events) factors. This exclusion from the MFD is unfortunate.

Aquatic Biological Conceptual Model description is good; quite complete treatment for lower trophic levels.

Lack of specification of model grid and process selection/representation are weaknesses of the MFD.

The MFD does not address how HSPF will predict past PCB loadings for long-term confirmation (hindcast) simulations, nor does it address how remedial action in the Rest-of-River study area will be represented in the different models.

QAPP: Tandem application of AQUATOX and EFDM is not presented in QAPP Section 4.8. Specific comparisons (QAPP, 4.7.1) are not defined: what spatial and temporal resolution; how will data be aggregated? What is the objective of this comparison?

IV. Concluding Comments

Clarification of transcript exchange with Dr. Lick regarding Question 4 (i.e., rigor):

When I commented that there was little "rigor" in the equilibrium partitioning calculation for PCBs and other hydrophobic organic chemicals (HOCs), I was referring to the analogy that is made between n-octanol, organic carbon, and lipid phases. Although it can be argued and is, in fact, often observed that chemical partitioning from water into octanol approximates the partitioning of that chemical into organic carbon and lipid, by definition an approximation is not "rigorous". So when a model is filled with estimates of equilibrium partitioning (to sediment, plankton, fish, etc.) that are based on correlations to the octanol-water partition coefficient, these estimates are not rigorous either. According to Thomann et al. (1992):

> Partitioning of organic chemicals into aquatic organisms is governed *to first order* by the lipid pool of the organism.

and:

> The tendency for organic chemicals to partition into lipid and organic carbon pools is *broadly represented* by the octanol/water partition coefficient ... *to first approximation*, the preference for chemicals to partition to octanol, lipid, and organic carbon is considered identical.

The analogy between octanol, organic carbon, and lipid is an extremely powerful approximation for models of HOC transpor, fate, and bioaccumulation. Claims as to it's rigor are questionable, however.

REFERENCES

De Boer, J., Van der Valk, F., Kerkhoff, M.A.T. and P. Hagel (1994) 8-year study of the elimination of PCBs and other organochlorine compounds from eel under natural conditions. Environ.Sci.Technol., 28:13, pp 2242-2248.

Eadie, B. J., N. R. Moorehead and P. F. Landrum. (1990) Three-phase partitioning of hydrophobic organic compounds in Great Lakes waters. Chemosphere 20(1-2):161-178.

Gailani,J., Lick, W., Ziegler, K. and D. Endicott. 1996. Development and validation of a fine-grained sediment transport model for the Buffalo River. Journal of Great Lakes Research, 22(3): 765-778.

Gobas, F.A.P.C. (1993) A model for predicting the bioaccumulation of hydrophobic organic chemicals in aquatic food webs: Application to Lake Ontario. Ecological Modeling, 69: pp. 1-17.

Gong, Y. and J.V. DePinto (1998) Desorption rates of two PCB congeners from suspended sediments - II. Model simulation. Wat. Res. 32:8, pp. 2518-2532.

Nordstrom, R.J., McKinnon, A.E. and A.S.W. De Freitas (1976) A bioenergetics-based model for pollutant accumulation by fish. Simulation of PCB and methylmercury levels in Ottowa River yellow perch. J. Fish. Res. Board Can., 33, pp.248-267.

Sijm, D.T.H.M., Seinen, W. and A. Opperhuizen (1992) Life-cycle biomagnification study in fish. Environ.Sci.Technol., 26, pp.2162-2174.

Sijm, D.T.H.M. and A. Van der Linde (1995) Size-dependent bioconcentration kinetics of hydrophobic organic chemicals in fish based on diffusive mass transfer and allometric relationships. Environ.Sci.Technol., 29, pp.2769-2777..

Skoglund, R.S. and D.L. Swackhamer.(1999) Evidence for the use of organic carbon as the sorbing matrix in the modeling of PCB accumulation in phytoplankton. Environ.Sci.Technol., 33:9, pp.1516-1519.

Song, J., DePinto, J.V. and J.F. Atkinson (1997) Incorporation of two-stage sorption kinetics into sediment and HOC transport models. Presented at the 40th Conference on Great Lakes Research, International Association for Great Lakes Research, Buffalo State College, Buffalo, N.Y. June 1-5, 1997.

Thomann, R. V. and J. P. Connolly. 1984. Model of PCB in the Lake Michigan Lake Trout food chain. Environ. Sci. Technol. 18(2):65-71.

Thomann, R. V. 1989. Bioaccumulation model of organic chemical distribution in aquatic fodd chains. Environ. Sci. Technol. 23(6):699-707.

Thomann, R.V., Connolly, J.P. and T.F. Parkerton (1992) An equilibrium model of organic chemical accumulation in aquatic food webs with sediment interaction. Environ. Sci. Technol. 11, pp. 615-629.

Velleux, M. and D. Endicott. 1996. Long-term Simulation of PCB Export from the Fox River to Green Bay. Journal of Great Lakes Research, 21(3):359-372.

Weinenger, D., D.A. Armstrong, and D.L. Swackhamer. 1983. Application of a sediment dynamics model for estimation of vertical burial rates of PCBs in southern Lake Michigan. in Physical behavior of PCBs in the Great Lakes. Mackay, D., Paterson, S., Eisenreich, S.J., and M.S. Simmons, eds. Ann Arbor Science Publishers. Ann Arbor, Michigan.

Wu, S.C. and P.M. Gschwend (1986) Sorption kinetics of hydrophobic organic compounds to natural sediments and soils. Environ. Sci. Technol. 20, pp 717-725.

Wu, S.C. and P.M. Gschwend (1988) Numerical modeling of sorption kinetics of hydrophobic organic compounds to soils and sediment particles. Water Resour. Res. 24:8, pp 1373-1383.